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Analytical Evaluation of Multicenter Integrals of r_{12}^{-1} with Slater-Type Atomic Orbitals. I. (1–2)-Type Three-Center Integrals*

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The three-center integral of r_{12}^{-1}, with one electron on one center in a Slater-type orbital, the second electron on two centers described by a product of Slater-type orbitals, is evaluated analytically. The result is an infinite sum in which the internuclear angles appear in spherical harmonics and the internuclear distances appear in modified spherical Bessel functions and exponential-type integrals. When one of the internuclear distances goes to zero, the two-center hybrid integral is obtained as a finite sum. The main mathematical techniques used to evaluate the integrals are the Fourier-transform convolution theorem, expansion of a Slater-type orbital on one center about another, coupling properties of spherical harmonics, and contour integration.

INTRODUCTION

The central problem of *a priori* molecular electronic calculations is the evaluation of multicenter integrals. Currently multicenter integrals of r_{12}^{-1} with Slater-type atomic orbitals (STO's) are evaluated numerically by three main methods: The Gaussian transform method,[1–5] the "polished brute-force method,[6–9] and methods based on the expansion of all STO's about a common center.[10–22] All these methods use extensive numerical integration techniques.

The purpose of this series of papers is to develop purely analytical formulas for multicenter integrals of r_{12}^{-1} with Slater-type orbitals. These formulas involve infinite summations but no numerical integrations. The analytical method, which has been sketched in a brief communication,[23,24] is a blend of (i) the Fourier-transform convolution theorem, (ii) expansion of a STO on one center about another, (iii) angular integrations over products of spherical harmonics only, and (iv) resolution of "radial integrations" with contour integration techniques.

This paper deals explicitly with the simplest multicenter integral,

$$I_{n_cl_cm_c\zeta_c;n_al_am_a\zeta_a,n_bl_bm_b\zeta_b}(\mathbf{R},\boldsymbol{\mathfrak{R}})$$

$$\equiv (N_aN_bN_c)^{-1}\int dV_1dV_2\Psi^*_{n_cl_cm_c\zeta_c}(\mathbf{r}_1)r_{12}^{-1}$$

$$\times\Psi^*_{n_al_am_a\zeta_a}(\mathbf{r}_2-\mathbf{R})\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}_2-\mathbf{R}-\boldsymbol{\mathfrak{R}}),\quad(1)$$

$$=I_{c;a,b},\quad(2)$$

where $\Psi_{nlm\zeta}(\mathbf{r})$ denotes a STO,

$$\Psi_{nlm\zeta}=Nr^{n-1}\exp(-\zeta r)Y_l^m(\theta,\phi),\quad(3)$$

N a normalization constant (whose value is irrelevant here), and $Y_l^m(\theta,\phi)$ a spherical harmonic. Throughout this paper, it is assumed that the n of each STO is an integer and that

$$n\geq l+1.\quad(4)$$

One electron is described by a STO located at the origin, the second by a product of STO's located at $\mathbf{R}$ and $\mathbf{R}+\boldsymbol{\mathfrak{R}}$ [thus the name (1–2)-type three-center integral]. Later papers will deal with (2–2)-type three-center integrals and with four-center integrals, but the basic techniques for evaluating the integrals are developed in this paper. The analytical formulas for calculating $I_{c;a,b}$ [Eqs. (1) and (2)] are given by Eqs. (31), (59), and (60). An extra dividend of the analytical approach is a fairly compact formula for two-center hybrid integrals, Eqs. (31) and (72).

FORMULATION

In this section the single six-dimensional integral (1) is reduced to an infinite number of one-dimensional integrals.

The six-dimensional integral (1) can be replaced immediately by a three-dimensional integral by virtue

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of the Fourier transform convolution theorem,[25–32]

$$I_{c;a,b}=(2\pi)^{-3}\int d^3\mathbf{k}F^*_{n_cl_cm_c\zeta_c}(k)(4\pi k^{-2})\times G_{n_al_am_a\zeta_a;n_bl_bm_b\zeta_b}(\mathbf{k},\boldsymbol{\mathfrak{R}})\exp(i\mathbf{k}\cdot\mathbf{R}). \quad (5)$$

The F and G, the Fourier transforms of the charge distributions of electrons 1 and 2, are defined by

$$F_{nlm\zeta}(\mathbf{k})\equiv N^{-1}\int dV\exp(i\mathbf{k}\cdot\mathbf{r})\Psi_{nlm\zeta}(\mathbf{r}), \quad (6)$$

$$G_{n_al_am_a\zeta_a;n_bl_bm_b\zeta_b}(\mathbf{k},\boldsymbol{\mathfrak{R}})\equiv(N_aN_b)^{-1}\int dV\exp(i\mathbf{k}\cdot\mathbf{r})\Psi^*_{n_al_am_a\zeta_a}(\mathbf{r})\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}-\boldsymbol{\mathfrak{R}}). \quad (7)$$

The $F_{nlm\zeta}(\mathbf{k})$ is readily evaluated[31]:

$$F_{nlm\zeta}(\mathbf{k})=f_{nl\zeta}(k)Y_l^m(\theta_k,\phi_k), \quad (8)$$

$$f_{nl\zeta}(k)=2\pi i^{l-1}(-d/d\zeta)^{n-l}(-k)^l(k^{-1}d/dk)^lk^{-1}\times[(\zeta-ik)^{-1}-(\zeta+ik)^{-1}]. \quad (9)$$

The spherical coordinates of $\mathbf{k}$ are denoted by (k,θ_k,ϕ_k). Note that when k is real,

$$f^*_{nl\zeta}(k)=(-1)^lf_{nl\zeta}(k), \qquad (k\text{ real}). \quad (10)$$

To evaluate the Fourier transform of the two-center distribution, first expand $\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}-\boldsymbol{\mathfrak{R}})$ about the origin[19]:

$$N_b^{-1}\Psi_{n_bl_bm_b\zeta_b}(\mathbf{r}-\boldsymbol{\mathfrak{R}})=\sum_{l=0}^{\infty}\sum_{\lambda=|l-l_b|}^{l+l_b}v_{l\lambda l_b}{}^{(n_b\zeta_b)}(r,\mathfrak{R})\sum_{m=-l}^{l}\left(\frac{2\lambda+1}{4\pi}\right)^{1/2}c^\lambda(l_b,m_b;l,m)Y_\lambda{}^{m_b-m}(\theta_\mathfrak{R},\phi_\mathfrak{R})Y_l{}^m(\theta,\phi), \quad (11)$$

$$v_{l\lambda l_b}{}^{(n_b\zeta_b)}(r,\mathfrak{R})=4\pi(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathscr{I}_l(\zeta_br)\mathscr{K}_\lambda(\zeta_b\mathfrak{R}), \qquad (r<\mathfrak{R}), \quad (12)$$

$$=(-1)^{l+\lambda}4\pi(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathscr{K}_l(\zeta_br)\mathscr{I}_\lambda(\zeta_b\mathfrak{R}), \qquad (r>\mathfrak{R}). \quad (13)$$

Here $(\mathfrak{R},\theta_\mathfrak{R},\phi_\mathfrak{R})$ denote the spherical coordinates of $\boldsymbol{\mathfrak{R}}$, $c^\lambda(l_b,m_b;l,m)$ the Condon–Shortley coefficients,[33]

$$\left(\frac{2\lambda+1}{4\pi}\right)^{1/2}c^\lambda(l_b,m_b;l,m)=\int d\Omega Y_\lambda{}^{m_b-m*}(\theta,\phi)Y_l{}^{m*}(\theta,\phi)Y_{l_b}{}^{m_b}(\theta,\phi), \quad (14)$$

and $\mathscr{I}$ and $\mathscr{K}$ denote modified spherical Bessel functions,[34a]

$$\mathscr{I}_l(x)=x^l(x^{-1}d/dx)^lx^{-1}\sinh x, \quad (15)$$

$$\mathscr{K}_l(x)=(-x)^l(x^{-1}d/dx)^lx^{-1}\exp(-x). \quad (16)$$

For $\exp(i\mathbf{k}\cdot\mathbf{r})$ in Eq. (7), the expansion,[34b]

$$\exp(i\mathbf{k}\cdot\mathbf{r})=4\pi\sum_{\Lambda=0}^{\infty}\sum_{M=-\Lambda}^{\Lambda}i^\Lambda j_\Lambda(kr)Y_\Lambda{}^M(\theta_k,\phi_k)Y_\Lambda{}^{M*}(\theta,\phi), \quad (17)$$

where j_Λ is a spherical Bessel function,[34c]

$$j_\Lambda(x)=(-x)^\Lambda(x^{-1}d/dx)^\Lambda x^{-1}\sin x, \quad (18)$$

is useful. With Eqs. (11)–(13) and (17) substituted into Eq. (7), and with the angular integration carried out via Eq. (14), G becomes

$$G_{n_al_am_a\zeta_a;n_bl_bm_b\zeta_b}(\mathbf{k},\boldsymbol{\mathfrak{R}})=\sum_{l=0}^{\infty}\sum_{\lambda=|l-l_b|}^{l+l_b}\sum_{m=-l}^{l}\sum_{\Lambda=|l-l_a|}^{l+l_a}[(2\lambda+1)(2\Lambda+1)]^{1/2}c^\lambda(l_b,m_b;l,m)c^\Lambda(l,m;l_a,m_a)\times Y_\lambda{}^{m_b-m}(\theta_\mathfrak{R},\phi_\mathfrak{R})Y_\Lambda{}^{m-m_a}(\theta_k,\phi_k)G_{l\lambda l_b\Lambda}{}^{n_a\zeta_an_b\zeta_b}(k,\mathfrak{R}), \quad (19)$$

where

$$G_{l\lambda l_b\Lambda}{}^{n_a\zeta_an_b\zeta_b}(k,\mathfrak{R})=i^\Lambda\int_0^\infty drj_\Lambda(kr)r^{n_a+1}\exp(-\zeta_ar)v_{l\lambda l_b}{}^{n_b\zeta_b}(r,\mathfrak{R}). \quad (20)$$

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The integration of Eq. (20) can be carried out in terms of the exponential-type integral,[34d]

$$E_n(x)=\int_1^\infty dt\, t^{-n}\exp(-xt), \quad (21)$$

$$=\alpha_{-n}(x), \quad (22)$$

and a singularityless version of E_n,

$$\tilde{E}_n(x)=E_n(x)+(-x)^{n-1}[\log x-\psi(n)]/(n-1)!, \quad (n-1\geq 0), \quad (23)$$

$$=E_n(x)-x^{n-1}(-n)!, \quad (n\leq 0), \quad (24)$$

$$=\hat{\alpha}_{-n}(x), \quad (25)$$

where[34e]

$$\psi(n)=(d/dn)\log\Gamma(n). \quad (26)$$

Note particularly that $\tilde{E}_n(x)$ has no singularities in the finite x plane. The $\tilde{E}_n$ differs slightly from the $\hat{E}_n$ used previously[23] by the author, but has the advantage of having the same differentiation law as E_n:

$$(-d/dx)E_n(x)=E_{n-1}(x), \quad (27)$$

$$(-d/dx)\tilde{E}_n(x)=\tilde{E}_{n-1}(x). \quad (28)$$

Note also that the asymptotic behavior of $E_n(x)$ for large $|x|$ is given by[34f]

$$E_n(x)\sim x^{-1}\exp(-x), \quad |x|\rightarrow\infty. \quad (29)$$

The result for G is then

$$\begin{aligned}G_{t\lambda l_b\Lambda}{}^{n_a\zeta_a n_b\zeta_b}(k,\mathfrak{R})=&\,2\pi i^{\Lambda-1}(-1)^{\Lambda+l+l_b}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\\&\times\mathcal{J}_\lambda(\zeta_b\mathfrak{R})\zeta_b^{l}(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}k^{\Lambda}(k^{-1}d/dk)^{\Lambda}k^{-1}\mathfrak{R}^{n_a-\Lambda-l}\\&\times\{E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-ik)\mathfrak{R}]-E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+ik)\mathfrak{R}]\}\\&+\pi i^{\Lambda-1}(-1)^{\Lambda}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\\&\times\mathcal{K}_\lambda(\zeta_b\mathfrak{R})\zeta_b^{l}(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}k^{\Lambda}(k^{-1}d/dk)^{\Lambda}k^{-1}\mathfrak{R}^{n_a-\Lambda-l}\\&\times\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-ik)\mathfrak{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+ik)\mathfrak{R}]\\&-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-ik)\mathfrak{R}]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+ik)\mathfrak{R}]\}. \quad (30)\end{aligned}$$

Substitution in Eq. (5) for $I_{c;a,b}$ of F and G in the forms of Eqs. (8), (10), and (19) and expansion of $\exp(i\mathbf{k}\cdot\mathbf{R})$ [Eq. (17)] permit the angular integration again to be carried out via Eq. (14) to yield for $I_{c;a,b}$

$$\begin{aligned}I_{c;a,b}=(-1)^{l_c}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{\lambda=|l-l_b|}^{l+l_b}\sum_{\Lambda=|l-l_a|}^{l+l_a}\sum_{t=|\Lambda-l_c|}^{\Lambda+l_c}&[(2\lambda+1)(2\Lambda+1)(2t+1)\pi^3]^{1/2}c^{\lambda}(l_bm_b;\,l,m)c^{\Lambda}(lm;\,l_am_a)\\&\times c^{t}(\Lambda,m-m_a;\,l_cm_c)Y_\lambda^{m_b-m}(\theta_{\mathfrak{R}},\phi_{\mathfrak{R}})Y_t^{m-m_a-m_c}(\theta_R,\phi_R)I_{c;a,b}{}^{t\lambda\Lambda}, \quad (31)\end{aligned}$$

where

$$I_{c;a,b}{}^{t\lambda\Lambda}=\pi^{-3}i^{t}\int_0^\infty dk f_{n_cl_c\zeta_c}(k)j_t(kR)G_{t\lambda l_b\Lambda}{}^{n_a\zeta_a n_b\zeta_b}(k,\mathfrak{R}), \quad (32)$$

and where (R,θ_R,ϕ_R) denote the spherical coordinates of $\mathbf{R}$. The evaluation of $I_{c;a,b}$ is thus replaced by the problem of evaluating the one-dimensional integrals $I_{c;a,b}{}^{t\lambda\Lambda}$ of Eq. (32).

PRELIMINARY MANIPULATIONS. GENERALIZED PRINCIPLE VALUE

$I_{c;a,b}{}^{t\lambda\Lambda}$ is not quite in a convenient form for evaluation. In this section some simple manipulations break $I_{c;a,b}{}^{t\lambda\Lambda}$ into convenient parts.

First note that the integrand of Eq. (32) is an even function of k, so that

$$\int_0^\infty\cdots dk=\frac{1}{2}\int_{-\infty}^{\infty}\cdots dk. \quad (33)$$

Next note that

$$i^t\int_{-\infty}^{\infty}j_t(kR)\cdots dk$$

$$=-\frac{1}{2}\int_{-\infty}^{\infty}[\mathcal{K}_t(-ikR)+(-1)^t\mathcal{K}_t(ikR)]\cdots dk. \quad (34)$$

Since the integrand is even, one of the $\mathcal{K}_t$'s may be disregarded and the other multiplied by 2. Examination of the integrand as $k\rightarrow 0$, however, shows that

$$\mathcal{K}_t(-ikR)f_{n_cl_c\zeta_c}(k)G_{t\lambda l_b\Lambda}{}^{n_a\zeta_a n_b\zeta_b}(k,\mathfrak{R})\sim k^{l_c+\Lambda-t-1}, \quad (k\rightarrow 0) \quad (35)$$

so that when t takes on its maximum value $(l_c+\Lambda)$, the left-hand side of Eq. (35) has a simple pole at the origin. As a consequence, when one of the $\mathcal{K}$'s is dropped in Eq. (34), the principle value[35] of the integral must be taken:

$$\int_{-\infty}^{\infty} j_t(kR)\cdots dk = -i^{-t}\mathcal{P}\int_{-\infty}^{\infty} \mathcal{K}_t(-ikR)\cdots dk. \quad (36)$$

In some of the manipulations below, poles at $k=0$ or higher order than the first are introduced into the integrand. The principal value, which is usually defined only for simple poles, must be generalized by the following definition for poles of order n:

$$\mathcal{P}\int_{-\infty}^{\infty} k^{-n}\cdots dk \equiv \int_{-\infty}^{\infty} (k\pm i\epsilon)^{-n}\cdots dk \pm \frac{1}{2}\oint^{(0^+)} k^{-n}\cdots dk \quad (37)$$

where ϵ is a small number (whose phase is such that $k=-i\epsilon$ is to the right of the integration path), and $\oint^{(0^+)}dk$ denotes an integral in the complex plane along a small circle enclosing the origin. It is easily seen that the definition (37) agrees with a notion of $\mathcal{P}k^{-1}$ as a generalized function[36] by differentiating the well-known relation

$$\mathcal{P}k^{-1} = (k\pm i\epsilon)^{-1} \pm i\pi\delta(k) \quad (38)$$

$(n-1)$ times to obtain

$$\mathcal{P}k^{-n} \equiv (-d/dk)^{n-1}\mathcal{P}k^{-1}/(n-1)!, \quad (39)$$

$$\mathcal{P}k^{-n} = (k\pm i\epsilon)^{-n} \pm i\pi(-1)^{n-1}\delta^{(n-1)}(k)/(n-1)!, \quad (40)$$

where

$$\delta^{(m)}(k) \equiv (d/dk)^m\delta(k) \quad (41)$$

is the mth derivative of the Dirac delta function.[36] The equivalence,

$$\int_{-\infty}^{\infty} i\pi(-1)^{n-1}\delta^{(n-1)}(k)\frac{1}{(n-1)!}\cdots dk = \frac{1}{2}\oint^{(0^+)} k^{-n}\cdots dk, \quad 42)$$

follows immediately from Cauchy's Integral Theorem.[35]

With Eqs. (33)–(37), Eq. (32) becomes

$$I_{c;a,b}{}^{tl\lambda\Lambda} = -\tfrac{1}{2}\pi^{-3}\mathcal{P}\int_{-\infty}^{\infty} dk f_{n_c l_c \zeta_c}(k) \times\mathcal{K}_t(-ikR)G_{l\lambda l_b\Lambda}{}^{n_a\zeta_a n_b\zeta_b}(k,\mathcal{R}). \quad (43)$$

With Eqs. (9) and (30) substituted for the f and G functions and with the substitution $k=ix$, Eq. (43) becomes

$$I_{c;a,b}{}^{tl\lambda\Lambda} = I^{(1)} + I^{(2)}, \quad (44)$$

$$\begin{aligned} I^{(1)} = {}& 2i\pi^{-1}(-1)^{\Lambda+l+l_b+l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\mathcal{G}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1} \\ & \times\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_t(xR)\left\{x^{l_c}\left(x^{-1}\frac{d}{dx}\right)^{l_c} x^{-1}[(\zeta_c-x)^{-1}-(\zeta_c+x)^{-1}]\right\} \\ & \times x^{\Lambda}(x^{-1}d/dx)^{\Lambda}x^{-1}\mathcal{R}^{n_a-\Lambda-l}\{E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)\mathcal{R}] - E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]\}, \end{aligned} \quad (45)$$

$$\begin{aligned} I^{(2)} = {}& i\pi^{-1}(-1)^{\Lambda+l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b^{-1}d/d\zeta_b)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1} \\ & \times\mathcal{P}\int_{i\infty}^{-i\infty} dx\mathcal{K}_t(xR)\left\{x^{l_c}\left(x^{-1}\frac{d}{dx}\right)^{l_c} x^{-1}[(\zeta_c-x)^{-1}-(\zeta_c+x)^{-1}]\right\} x^{\Lambda}\left(x^{-1}\frac{d}{dx}\right)^{\Lambda} x^{-1}\mathcal{R}^{n_a-\Lambda-l} \\ & \times\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)\mathcal{R}] - \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+x)\mathcal{R}] - \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}] + \tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)\mathcal{R}]\}. \end{aligned} \quad (46)$$

The two parts $I^{(1)}$ and $I^{(2)}$ of $I_{c;a,b}{}^{tl\lambda\Lambda}$ are evaluated individually in the next section.

EVALUATION OF $I^{(1)}$ AND $I^{(2)}$

The remaining integration in $I^{(1)}$ and $I^{(2)}$ is carried out most easily by the powerful technique of contour integration.[35] Depending on the behavior of each term in the integrand, the contour can be "closed" at infinity in either the left or right half-plane and the term evaluated by the residue theorem.[35] Since the sign of $R-\mathcal{R}$ determines in which half-plane some of the terms go to zero, the formula for the integrals has a two-part form.

Consider first $I^{(1)}$ in the case $\mathcal{R}>R$. From Eqs. (45), (16), and (29) one sees that the term proportional to $E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)\mathcal{R}]$ goes to zero exponentially fast as $\mathrm{Re}(x)\rightarrow\infty$. For this term the contour can be closed along a large semicircle in the right half-plane. The contour then encloses two singularities: a pole at $x=+\zeta_c$ and "$\frac{1}{2}$" of a pole at $x=0$ [cf. Eq. (37)]. Similarly, the contour of the term with $E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]$ can be closed in the left half-plane enclosing a pole at $x=-\zeta_c$ and "$\frac{1}{2}$" of a pole at $x=0$. The value of integral is then just $(\pm 2\pi i)$ times the sum of the residues at $x=\pm\zeta_c$ and 0. The residues at $x=\pm\zeta_c$ are taken after integrating

[35] See, e.g., G. F. Carrier, M. Krook, and C. E. Pearson, *Functions of a Complex Variable* (McGraw-Hill Book Co., New York, 1966).
[36] See, e.g., M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions* (Cambridge University Press, London, 1958).

by parts l_c times to obtain simple poles. There is a nonzero residue at the origin only when $t=\Lambda-l_c$. [Note that $t\geq|\Lambda-l_c|$.] The result is

$$I^{(1)}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{g}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times\left(-8(-1)^{\Lambda+l+l_b+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{g}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]\right.$$

$$\left.+\delta_{t,\Lambda-l_c}8(-1)^{\Lambda+l+l_b}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)![(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{\Lambda-l_c}\mathcal{R}^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}]\right),$$

$$(\mathcal{R}>\mathcal{R}).\quad(47)$$

Consider next $I^{(1)}$ when $\mathcal{R}<R$. Then $\mathcal{K}_t(xR)$ dominates the integrand of Eq. (45) taking the entire integrand to zero as $\mathrm{Re}(x)\rightarrow\infty$. But if the contour were "closed" at infinity in the right half-plane, the logarithmic branch cut [cf. Eq. (23)] of $E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]$, which runs from $x=\zeta_a+\zeta_b$ to $x=+\infty$, would cause difficulties. By a suitable trick, however, the logarithmic term can be clothed in a function which approaches zero sufficiently fast as $\mathrm{Re}(x)\rightarrow\infty$ to permit closure of the contour in the left half-plane (which is free of branch cuts). The trick is the identity,

$$(x^{-1}d/dx)^{\Lambda}x^{-1}\mathcal{R}^{n_a-\Lambda-l}\{E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)\mathcal{R}]-E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]\}$$

$$=(x^{-1}d/dx)^{\Lambda}x^{-1}\mathcal{R}^{n_a-\Lambda-l}\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]\}$$

$$+(x^{-1}d/dx)^{\Lambda}x^{-1}R^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]$$

$$+E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)R]-E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]\},\quad(48)$$

which follows from Eqs. (23) and (24) and the relation

$$(2\Lambda+1)>\Lambda+l-n_a.\quad(49)$$

When Eq. (48) is substituted into Eq. (45), all the $\tilde{E}$ terms and the $E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+x)R]$ term can be evaluated by a contour closed in the right half-plane [cf. Eqs. (16) and (29)], and the $E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]$ term, by a contour closed in the left half-plane. The result is similar to the $\mathcal{R}>R$ case for the E terms, there are extra contributions to the residues at $x=\pm\zeta_c$ from the $\tilde{E}$ terms, and there is an additional contribution to the residue at $x=0$ when $t=\Lambda+l_c$. The result is

$$I^{(1)}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{g}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times\left(-8(-1)^{\Lambda+l+l_b+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{g}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]\right.$$

$$+\delta_{t,\Lambda-l_c}8(-1)^{\Lambda+l+l_b}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)![(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{n_a-l-l_c}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R]$$

$$+4(-1)^{\Lambda+l+l_b}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}$$

$$\times\{\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]-\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)\mathcal{R}]$$

$$-R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]+R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)R]\}$$

$$+\delta_{t,\Lambda+l_c}8(-1)^{\Lambda+l+l_b+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c![(\Lambda+l_c)!(2\Lambda+1)!]^{-1}$$

$$\left.\times R^{-1-\Lambda-l_c}\{\mathcal{R}^{n_a+\Lambda-l+1}\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}]-R^{n_a+\Lambda-l+1}\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R]\}\right),\quad(\mathcal{R}<R).\quad(50)$$

For $I^{(2)}$, the case $\mathcal{R}<R$ is easier. The $\mathcal{K}_t(xR)$ takes the integrand of Eq. (46) to zero exponentially fast as $\mathrm{Re}(x)\rightarrow\infty$, the $\tilde{E}$ functions have no singularities in the finite plane, and the integral is $(2\pi i)$ times the residue at $x=\zeta_c$ plus (πi) times the residue at $x=0$ (which is nonzero only when t takes its maximum value, $\Lambda+l_c$). The

result is

$$I^{(2)}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$(2(-1)^{\Lambda}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}$$

$$\times\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)\mathcal{R}]$$

$$+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-\zeta_c)\mathcal{R}]\}+\delta_{t,\Lambda+l_c}4(-1)^{\Lambda+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c![(\Lambda+l_c)!(2\Lambda+1)!]^{-1}$$

$$\times R^{-1-\Lambda-l_c}\mathcal{R}^{n_a+\Lambda-l+1}\{\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}]-\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)\mathcal{R}]\}),\qquad(\mathcal{R}<R).\tag{51}$$

The evaluation of $I^{(2)}$ when $\mathcal{R}>R$ is more complicated. From Eqs. (46), (23), (29), and (16), it is seen that each $\tilde{E}_n$ is the sum of an E_n, which dominates the $\mathcal{K}_t$ at infinity, and a logarithmic term, which is dominated by the $\mathcal{K}_t$. Moreover, the branch point of $E_n[(\zeta_a-\zeta_b-x)\mathcal{R}]$ can lie either on the positive or negative real axis, depending on the sign of $\zeta_a-\zeta_b$. Avoidance of the pitfalls which follow from these considerations requires some extra manipulations.

To begin, the terms in the integrand of $I^{(2)}$ with $\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a\pm\zeta_b+x)\mathcal{R}]$ go to zero in the right half-plane, have singularities only at $x=0$ and $+\zeta_c$, and can be evaluated as before. For the terms involving $\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a\pm\zeta_b-x)\mathcal{R}]$, we first indent the integration path so that it crosses the negative real axis to the left of all the singularities of the integrand. In so deforming the contour we pick up residues at $x=0$ and $-\zeta_c$. Thus,

$$I^{(2)}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times(-4(-1)^{\Lambda+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{G}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}$$

$$\times\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]\}+\delta_{t,\Lambda-l_c}4(-1)^{\Lambda}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)!$$

$$\times[(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{\Lambda-l_c}\mathcal{R}^{n_a-\Lambda-l}\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)\mathcal{R}]\})+I^{(2)}{}_{\text{left}},\quad(\mathcal{R}>R),\tag{52}$$

where

$$I^{(2)}{}_{\text{left}}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times i\pi^{-1}(-1)^{\Lambda+l_c}\int^{(i\infty,-\gamma^+,-i\infty)}dx\mathcal{K}_t(xR)\left\{x^{l_c}\left(x^{-1}\frac{d}{dx}\right)^{l_c}x^{-1}[(\zeta_c-x)^{-1}-(\zeta_c+x)^{-1}]\right\}$$

$$\times x^{\Lambda}(x^{-1}d/dx)^{\Lambda}x^{-1}\mathcal{R}^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)\mathcal{R}]\},\tag{53}$$

and the real number γ satisfies

$$\zeta_a+\zeta_b+\zeta_c<\gamma<\infty.\tag{54}$$

(If the $\tilde{E}_n$ were E_n, and if $\zeta_a>\zeta_b$, the integration path in $I^{(2)}{}_{\text{left}}$ could be closed to the left and $I^{(2)}{}_{\text{left}}$ would vanish.)

Next, we use Eqs. (23) and (24) and the relation

$$(2l+1)>2l-(n_a-l_a)\geq\Lambda+l-n_a,\tag{55}$$

to justify the identity,

$$(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}\mathcal{R}^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)\mathcal{R}]\}$$

$$=(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}\mathcal{R}^{n_a-\Lambda-l}\{-E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)\mathcal{R}]+E_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)\mathcal{R}]\}$$

$$+(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}R^{n_a-\Lambda-l}\{E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]-E_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)R]$$

$$-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)R]\}.\tag{56}$$

In Eq. (56) we require that, regardless of the sign of $\zeta_a-\zeta_b$, the branch cut in both $E_n[(\zeta_a-\zeta_b-x)\mathcal{R}]$ and $E_n[(\zeta_a-\zeta_b-x)R]$ run from $x=\zeta_a-\zeta_b$ to $x=+\infty+i\epsilon$. When Eq. (56) is substituted into Eq. (53), the terms involving the E_n vanish fast enough to permit closure of the contour to the left, which leads to a zero contribution to $I^{(2)}{}_{\text{left}}$. The terms involving the $\tilde{E}_n$ permit closure in the right half-plane, and since there are only poles in the right half-plane,

$$I^{(2)}{}_{\text{left}}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times i\pi^{-1}(-1)^{\Lambda+l_c}\oint^{(-\gamma^+,\gamma^+)}dx\mathcal{K}_t(xR)\{x^{l_c}(x^{-1}d/dx)^{l_c}x^{-1}[(\zeta_c-x)^{-1}-(\zeta_c+x)^{-1}]\}$$

$$\times x^{\Lambda}(x^{-1}d/dx)^{\Lambda}x^{-1}R^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-x)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-x)R]\},\qquad(\mathcal{R}>R).\quad(57)$$

Finally, $I^{(2)}{}_{\text{left}}$ becomes $(2\pi i)$ times the residues at $x=\pm\zeta_c$ and $x=0$. The residues at the origin are nonzero only when $t=\Lambda\pm l_c$. Thus

$$I^{(2)}{}_{\text{left}}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times\Big(2(-1)^{\Lambda}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}$$

$$\times\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-\zeta_c)R]\}+2(-1)^{l_c}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(-\zeta_cR)$$

$$\times(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)R]\}$$

$$+\delta_{t,\Lambda+l_c}4(-1)^{\Lambda+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c![(\Lambda+l_c)!(2\Lambda+1)!]^{-1}R^{n_a-l-l_c}$$

$$\times\{\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R]-\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)R]\}+\delta_{t,\Lambda-l_c}4(-1)^{l_c+t}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)!$$

$$\times[(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{n_a-l-l_c}\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)R]\}\Big),\qquad(\mathcal{R}>R).\quad(58)$$

MASTER FORMULA FOR $I_{c;a,b}{}^{tl\lambda\Lambda}$

If one substitutes Eqs. (50) and (51) for $I^{(1)}$ and $I^{(2)}$ into Eq. (44), one obtains for $I_{c;a,b}{}^{tl\lambda\Lambda}$, for $\mathcal{R}<R$,

$$I_{c;a,b}{}^{tl\lambda\Lambda}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{G}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times\Big(-8(-1)^{\Lambda+l+l_b+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{G}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]$$

$$+\delta_{t,\Lambda-l_c}8(-1)^{\Lambda+l+l_b}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)![(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{n_a-l-l_c}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R]$$

$$+4(-1)^{\Lambda+l+l_b}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\{\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]$$

$$-\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)\mathcal{R}]-R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]$$

$$+R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)R]\}$$

$$+\delta_{t,\Lambda+l_c}8(-1)^{\Lambda+l+l_b+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c!$$

$$\times[(\Lambda+l_c)!(2\Lambda+1)!]^{-1}R^{-1-\Lambda-l_c}\{\mathcal{R}^{n_a+\Lambda-l+1}\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}]-R^{n_a+\Lambda-l+1}\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R]\}\Big)$$

$$+\left(\frac{-d}{d\zeta_b}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$

$$\times\Big(2(-1)^{\Lambda}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]$$

$$-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)\mathcal{R}]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-\zeta_c)\mathcal{R}]\}$$

$$+\delta_{t,\Lambda+l_c}4(-1)^{\Lambda+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c![(\Lambda+l_c)!(2\Lambda+1)!]^{-1}R^{-1-\Lambda-l_c}$$

$$\times\mathcal{R}^{n_a+\Lambda-l+1}\{\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)\mathcal{R}]-\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)\mathcal{R}]\}\Big),\qquad(\mathcal{R}<R).\quad(59)$$

The $\mathcal{R}>R$ case, obtained from Eqs. (44), (47), (52), and (58), is

$$I_{c;a,b}{}^{t l\lambda\Lambda}=\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{g}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$
$$\times(-8(-1)^{\Lambda+l+l_b+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{g}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]$$
$$+\delta_{t,\Lambda-l_c}8(-1)^{\Lambda+l+l_b}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)![(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{\Lambda-l_c}\mathcal{R}^{n_a-\Lambda-l}E_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}])$$
$$+\left(\frac{-d}{d\zeta_c}\right)^{n_c-l_c}\left(\frac{-d}{d\zeta_b}\right)^{n_b-l_b}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b^{l}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l}\zeta_b^{-1}$$
$$\times(-4(-1)^{\Lambda+t}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{g}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}\mathcal{R}^{n_a-\Lambda-l}$$
$$\times\{\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]\}$$
$$+2(-1)^{\Lambda}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}$$
$$\times\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b-\zeta_c)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b-\zeta_c)R]\}$$
$$+2(-1)^{l_c}(\zeta_c^{-1}d/d\zeta_c)^{l_c}\zeta_c^{-1+\Lambda+l_c}\mathcal{K}_t(-\zeta_cR)(\zeta_c^{-1}d/d\zeta_c)^{\Lambda}\zeta_c^{-1}R^{n_a-\Lambda-l}$$
$$\times\{-\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]+\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)R]\}$$
$$+\delta_{t,\Lambda-l_c}4(-1)^{\Lambda}\zeta_c^{-2l_c-2}(\Lambda-l_c)!l_c!(2\Lambda)![(2\Lambda-2l_c+1)!\Lambda!]^{-1}R^{\Lambda-l_c}$$
$$\times\{\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}]-\mathcal{R}^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)\mathcal{R}]$$
$$-R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a+\zeta_b)R]+R^{n_a-\Lambda-l}\tilde{E}_{\Lambda+l+1-n_a}[(\zeta_a-\zeta_b)R]\}$$
$$+\delta_{t,\Lambda+l_c}4(-1)^{\Lambda+l_c}\zeta_c^{-2l_c-2}(2\Lambda+2l_c)!\Lambda!l_c![(\Lambda+l_c)!(2\Lambda+1)!]^{-1}R^{n_a-l-l_c}$$
$$\times\{\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a+\zeta_b)R]-\hat{\alpha}_{n_a+\Lambda-l}[(\zeta_a-\zeta_b)R]\}),\qquad(\mathcal{R}>R).\tag{60}$$

Equations (1), (31), (59), and (60) contain the definition and evaluation of (1–2)-type three-center integrals. There are no restrictions on the values of ζ_a, ζ_b, ζ_c, n_a, n_b, n_c, l_a, l_b, and l_c other than Eq. (4). Both R and $\mathcal{R}$, however, must be nonzero.

ON EXPANDING THE DERIVATIVES

Before Eqs. (31), (59), and (60) can be used to compute three-center integrals, the derivatives must be taken. Several relations which help simplify the differentiations are Eqs. (27), (28), and

$$\left(x^{-1}\frac{d}{dx}\right)^{l}x^{-1}=\sum_{m=0}^{l}(-1)^m(l+m)!\times[2^m m!(l-m)!]^{-1}x^{-l-m-1}\left(\frac{d}{dx}\right)^{l-m},\tag{61}$$

$$(d/dx)x^{-l}\mathcal{g}_l(x)=x^{-l}\mathcal{g}_{l+1}(x),\tag{62}$$

$$(d/dx)x^{l+1}\mathcal{g}_l(x)=x^{l+1}\mathcal{g}_{l-1}(x),\tag{63}$$

$$(d/dx)x^{-l}\mathcal{K}_l(x)=-x^{-l}\mathcal{K}_{l+1}(x),\tag{64}$$

and

$$(d/dx)x^{l+1}\mathcal{K}_l(x)=-x^{l+1}\mathcal{K}_{l-1}(x).\tag{65}$$

Equation (61) is easily proved by induction. Equations (62)–(65) follow from Eqs. (15) and (16) and are equivalent to those for spherical Bessel functions[34g]. When expanding the formulas (59) and (60), a variety of results can be obtained by using different mixtures of Eqs. (62)–(65). Which result will prove most useful is yet undetermined.

TWO-CENTER HYBRID INTEGRAL

The two-center hybrid integral, defined as $I_{c;a,b}$, with $R=0$, is easily obtained from Eqs. (60).

First note that if $t>0$, then

$$I_{c;a,b}{}^{tl\lambda\Lambda}(R=0)=0,\qquad(t>0),\tag{66}$$

which follows immediately from Eqs. (18) and (32). By examining the summation limits in Eq. (31), one finds that when

$$t=0,\qquad(R=0),\tag{67}$$

then

$$\Lambda=l_c,\qquad(R=0),\tag{68}$$

and

$$|l_a-l_c|\le l\le l_a+l_c,\qquad(R=0).\tag{69}$$

Note particularly that the inequality (69) implies Eq. (31) has only a *finite* number of terms.

Next consider the terms in Eq. (60) of the form

$$\mathcal{K}_0(\pm\zeta_cR)(\zeta_b^{-1}d/d\zeta_b)^{l}\zeta_b^{-1}R^{n_a-l-l_c}\times\{\text{odd function of }\zeta_bR\text{ analytic at }\zeta_bR=0\}.\tag{70}$$

The leading power of R in (70) is $R^{n_a+l-l_c}$. By virtue of the inequalities (69) and (4),

$$n_a+l-l_c\ge n_a+|l_c-l_a|-l_c>0,\tag{71}$$

so that such terms (70) vanish as $R\to 0$.

With the above considerations, one obtains[37] from

[37] Cf. K. Ruedenberg, C. C. J. Roothaan, and W. Jaunzemis, J. Chem. Phys. **24**, 201 (1956).

Eq. (60), with R set equal to zero,

$$
\begin{aligned}
I_{c;a,b}{}^{tl\lambda\Lambda}(R=0)=&\ \delta_{t,0}\delta_{\Lambda,l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathcal{J}_\lambda(\zeta_b\mathcal{R})\zeta_b{}^{l}(\zeta_b{}^{-1}d/d\zeta_b)^{l}\zeta_b{}^{-1}\\
&\times(-8(-1)^{l+l_b+l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}\mathcal{R}^{n_a-l_c-l}E_{l_c+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]\\
&\quad+8(-1)^{l+l_b+l_c}\zeta_c{}^{-2l_c-2}(2l_c)!\mathcal{R}^{n_a-l_c-l}E_{l_c+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}])\\
&\quad+\delta_{t,0}\delta_{\Lambda,l_c}(-d/d\zeta_c)^{n_c-l_c}(-d/d\zeta_b)^{n_b-l_b}(\zeta_b{}^{-1}d/d\zeta_b)^{l_b}\zeta_b{}^{l_b+1}\mathcal{K}_\lambda(\zeta_b\mathcal{R})\zeta_b{}^{l}(\zeta_b{}^{-1}d/d\zeta_b)^{l}\zeta_b{}^{-1}\\
&\times(-4(-1)^{l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}\mathcal{R}^{n_a-l_c-l}\\
&\times\{\tilde{E}_{l_c+l+1-n_a}[(\zeta_a+\zeta_b+\zeta_c)\mathcal{R}]+\tilde{E}_{l_c+l+1-n_a}[(\zeta_a-\zeta_b+\zeta_c)\mathcal{R}]\}\\
&\quad+4(-1)^{l_c}\zeta_c{}^{-2l_c-2}(2l_c)!\mathcal{R}^{n_a-l_c-l}\{\tilde{E}_{l_c+l+1-n_a}[(\zeta_a+\zeta_b)\mathcal{R}]-\tilde{E}_{l_c+l+1-n_a}[(\zeta_a-\zeta_b)\mathcal{R}]\}).
\end{aligned}
\tag{72}
$$

Equation (72) can be slightly simplified by use of

$$(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1+2l_c}(\zeta_c{}^{-1}d/d\zeta_c)^{l_c}\zeta_c{}^{-1}=\zeta_c{}^{-1}(d/d\zeta_c)^{2l_c}\zeta_c{}^{-1}, \tag{73}$$

$$=(2l_c+1)^{-1}[\zeta_c{}^{-1}(d/d\zeta_c)^{2l_c+1}-(d/d\zeta_c)^{2l_c+1}\zeta_c{}^{-1}]. \tag{74}$$

Thus, Eq. (72), along with Eqs. (69), (68), (67), (31), and (1), specifies the two-center hybrid integral.

SUMMARY

An analytical formula has been derived for (1–2)-type three-center integrals of $r_{12}{}^{-1}$ with integer-n Slater-type orbitals. The main steps in the derivation were (i) use of the Fourier-transform convolution theorem to reduce the six-dimensional integral to a three-dimensional one, (ii) evaluation of the Fourier transform of a two-center charge distribution as a multipole expansion, (iii) integration over angles of products of spherical harmonics only, and (iv) extensive manipulation of integration contours and use of the residue theorem. In the end, the integral (1) is expressed as an infinite sum [(Eq. (31)] of products of spherical harmonics of the internuclear position-vector angles times a function of the internuclear distances $\mathcal{R}$ and R. The radial function has a two-part form [Eqs. (59) and (60)], depending on the sign of $\mathcal{R}-R$, and it involves functions no more complicated than spherical Bessel functions (i.e., exponentials) and the exponential-type integral. The formulas are valid for general values of the quantum numbers and orbital exponents defining the Slater-type orbitals. The two-center hybrid integral is obtained as a special case [Eq. (72)] by setting $R=0$ in the three-center formula.

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Analytical Evaluation of Multicenter Integrals of $r_{12}{}^{-1}$ with Slater-Type Atomic Orbitals. II. Three-Center Nuclear-Attraction Integrals*

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The general three-center one-electron nuclear-attraction integral with integer-n Slater-type orbitals is evaluated analytically by letting the orbital exponent of a 1s orbital in the analytical formula for two-electron three-center electron-repulsion integrals tend to infinity. The result is an infinite sum in which the internuclear angles appear in spherical harmonics, and the internuclear distances appear in modified spherical Bessel functions and exponential-type integrals.

INTRODUCTION

In this second paper of a series[1] on multicenter integrals, a compact analytical formula is derived for three-center nuclear-attraction integrals with integer-n Slater-type atomic orbitals (STO's). Current methods for calculating three-center nuclear-attraction integrals usually involve numerical integration (although closed-form analytical expressions are known[2] for special cases)

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[1] H. J. Silverstone, J. Chem. Phys. **48,** 4098 1968 (preceding paper), hereafter referred to as I.

[2] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4,** 121 (1936).